

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



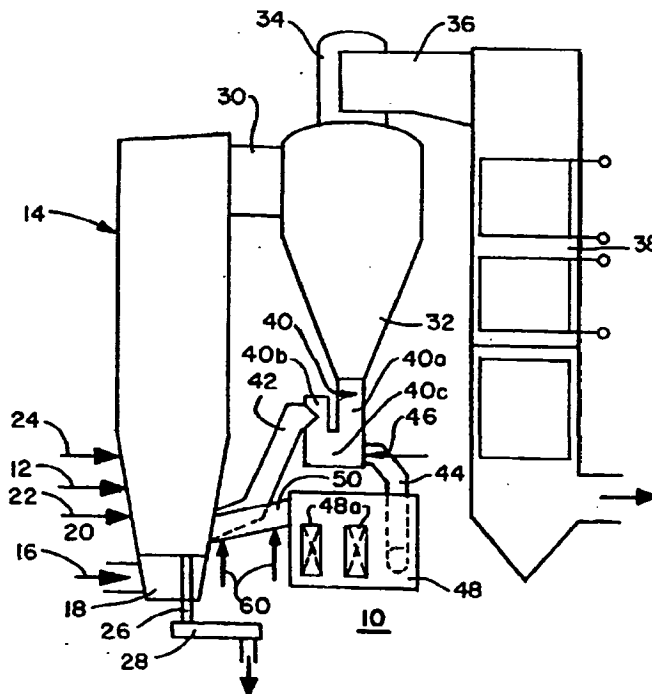
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B01J 20/34, B01D 53/50, F23C 11/02, F23L 7/00</b>		A1	(11) International Publication Number: <b>WO 97/06889</b>
			(43) International Publication Date: 27 February 1997 (27.02.97)
(21) International Application Number: PCT/IB96/00930		(81) Designated States: CA, CN, CZ, FI, KR, KZ, PL, RO, SE, TR.	
(22) International Filing Date: 29 July 1996 (29.07.96)		Published	
(30) Priority Data: 08/517,486 21 August 1995 (21.08.95) US		With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(71) Applicant: ABB RESEARCH LTD. [CH/CH]; Affolternstrasse 44, CH-8050 Zurich (CH).			
(71)(72) Applicant and Inventor (for KZ only): CHIU, John, H. [US/US]; 49 Parsons Drive, West Hartford, CT 06117 (US).			
(74) Agents: FOURNIER, Arthur, E., Jr. et al.; Combustion Engineering, Inc., Patent Services 4540-0426, 2000 Day Hill Road, Windsor, CT 06095 (US).			

(54) Title: A METHOD FOR REACTIVATING SORBENT TO ENABLE THE REUSE THEREOF

(57) Abstract

A method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO that is embodied in spent ash, which is generated as a consequence of the combustion in a fossil fuel-fired combustor (14) of fossil fuel in the presence of sorbent containing Ca. The sorbent containing unreacted CaO is subjected to steam having a predetermined temperature and a predetermined partial pressure operative to effect the conversion of the unreacted CaO to Ca(OH)<sub>2</sub> whereby a fracturing of the sorbent occurs such that the Ca(OH)<sub>2</sub> becomes exposed. Thereafter, the sorbent now containing Ca(OH)<sub>2</sub> is reinjected into the fossil fuel-fired combustor (14) at a temperature within the fossil fuel-fired combustor (14) operative to effect the re-conversion of the Ca(OH)<sub>2</sub> to CaO.



BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

A METHOD FOR REACTIVATING SORBENT  
TO ENABLE THE REUSE THEREOF

BACKGROUND OF THE INVENTION

5           This invention relates to SO<sub>2</sub> emission reduction and, more specifically, to a method for reactivating for purposes of the reuse thereof the sorbent, which is injected into a fossil fuel-fired combustor in order to effectuate the capture therewith of the SO<sub>2</sub> that is released during the combustion of the fossil fuel within the fossil fuel-fired combustor.

10           It has long been known in the prior art to employ a sorbent embodying CaO to effect therewith capture of the SO<sub>2</sub> that is released during the combustion of the fossil fuel within fossil fuel-fired combustors. Moreover, such sorbent has proven to be particularly effective in capturing the SO<sub>2</sub> that is released within a circulating fluidized bed combustor during  
15 the combustion therewithin of fossil fuels that are solid in nature. However, notwithstanding the fact that sorbent has proven to be particularly effective when utilized to accomplish the capture of SO<sub>2</sub> in circulating fluidized bed combustors, it has nevertheless been found that sorbent consumption and the need to effect the disposal of the ash, in  
20 which sorbent is contained, that is produced as a consequence of the combustion, which occurs within the circulating fluidized bed combustor, represent major operating costs to the operator of the circulating fluidized bed combustor. Furthermore, it is expected that these costs will continue

- 2 -

to escalate as environmental constraints become even more stringent in the future. Thus, in summary the increased calcium-to-sulfur mole ratio necessary to meet very high levels of sulfur removal will seriously impact the cost effectiveness of circulating fluidized bed technology unless the consumption of sorbent can be reduced.

In accordance with the process employed in circulating fluidized bed technology, fossil fuel, which may take any one of a number of different forms, e.g., coal, etc., is burned in the combustor of a circulating fluidized bed system in the presence of a sorbent embodying CaO, such sorbent being injected into the combustor in order that while the fossil fuel is being burned in the combustor such sorbent undergoes calcination and sulfation reactions. To this end, such sorbent, while the fossil fuel is being burned in the combustor, is operative to effect the capture of SO<sub>2</sub>. In doing so though, not all of the CaO in the sorbent is fully utilized for sulfur capture. This is attributable to the fact that in capturing the sulfur the CaO in the sorbent combines with the sulfur to form CaSO<sub>4</sub>. As such, because the specific volume of the CaSO<sub>4</sub> is greater than the specific volume of the CaO, the pore structure of the sorbent becomes plugged with CaSO<sub>4</sub>. That is, the surface of the CaO essentially becomes covered with an outer layer of CaSO<sub>4</sub>, which functions to effectively shield the unreacted free CaO in the interior of the particles of sorbent from further reaction with SO<sub>2</sub>, i.e., inhibits further capture of sulfur by the sorbent.

It has been known heretofore to reinject ash into the combustor of the circulating fluidized bed system in an effort to effect the reuse of the sorbent contained in the reinjected ash. This reinjection of ash containing sorbent eventually reaches a point of diminishing returns. Namely, the particles of sorbent eventually become sulfated and the internal pores of the sulfur become blocked by CaSO<sub>4</sub>. Accordingly, further sulfur capture by the sorbent can only occur if the CaO in the interior of the sorbent particles becomes exposed. Attempts, to which

- 3 -

reference will be had more fully hereinafter, have been made to effect such exposure of the CaO.

Thus, by way of summary, a substantial effort has been put forth heretodate in the prior art in an attempt to develop new methods for  
5 reducing sorbent consumption, diminishing solids waste disposal and improving solids waste utilization. In this regard, by way of exemplification and not limitation, reference is had to U.S. Patent No. 5,342,594 entitled "Fluidized Bed Process For SO<sub>x</sub> Removal," which issued on August 30, 1994. As taught in U.S. Patent No. 5,342,594, hot, unclean gases having  
10 gaseous sulphur oxide-containing impurities are mixed within a mixing chamber with a solid process material comprising CaCO<sub>3</sub> such that the gaseous sulphur oxide-containing impurities react with the CaCO<sub>3</sub> to form a solid impurity reaction product thereof. Thereafter, the solid process material and the solid impurity reaction product are separated from the  
15 unclean gases to provide purified gases. Whereupon, the separated solid impurity reaction product and solid process material are returned to the mixing chamber to be once again mixed with hot, unclean gases.

Also, further in this regard, reference is had, by way of exemplification and not limitation, to U.S. Patent No. 5,345,883 entitled  
20 "Reactivation Of Sorbent In A Fluid Bed Boiler," which issued on September 13, 1994. In accordance with the teachings of U.S. Patent No. 5,345,883, a jet of fracturing medium of liquid water or steam is injected at a sufficiently high pressure and in being so injected is directed so as to impinge upon sorbent particles containing unreacted sorbent material  
25 inside, whereby these sorbent particles are mechanically fractured to expose the unreacted sorbent contained therewithin. To this end, as taught in U.S. Patent No. 5,345,883, the fracturing medium when being so injected is at a temperature lower than the temperature of the sorbent particles that the fracturing medium is made to impinge upon such that the  
30 fracturing of the sorbent particles is the result of thermal shock. Or, as taught in U.S. Patent No. 5,345,883, the fracturing medium when being so

injected is directed at the sorbent particles such that the sorbent particles are caused to be mechanically broken apart by striking a target surface or other particles.

In addition, reference is had further in this regard, by way of exemplification and not limitation, to U.S. Patent No. 5,344,632 entitled "Method For Reducing Sulfur Oxides Emissions In A Combustion Process," which issued on September 6, 1994. As taught in U.S. Patent No. 5,344,632, the mixture of flue gases and entrained fine particles, a portion of which are particles of limestone, which are both unsulfated and have undergone chemical conversion to calcined limestone, are made to enter a humidifying reactor at a reduced temperature, wherein the reduced temperature results from heat having been previously extracted from the mixture. Thereafter, water is dispersed in the form of a plurality of fine water particles that evaporate and humidify the mixture of flue gases and entrained fine particles, which in combination with the reduced temperature of the mixture, is said to be highly conducive to the formation of a thin film of alkali solution of calcium hydroxide on the surface of the particles of limestone. This alkali solution is then effective in absorbing sulfur oxides present in the mixture of flue gases and entrained fine particles to form calcium sulfate and calcium sulfide precipitation.

Lastly, reference is had in this regard, by way of exemplification and not limitation, to U.S. Patent No. 5,341,753 entitled "Circulating Fluidized Bed Power Plant With Improved Mixing Of Sorbents With Combustion Gases," which issued on August 30, 1994. In accordance with the teachings of U.S. Patent No. 5,341,743, recognition is had therein of the fact that the calcium sulfur ratio required for a desired amount of sulfur removal is a function of how much excess particle density in the gas stream is required in order to ensure that a sufficient number of sulfur dioxide molecules come in contact with the calcium dioxide particles. Thus, it is said to be desirable to improve the contact between the calcium and the sulfur dioxide particles. To this end, high velocity

steam is injected into the circulating fluidized bed boiler to improve the mixing therewithin of the recirculating solids with the combustion gases whereby the circulating fluidized bed boiler for burning sulfur containing fuels is allegedly made to utilize limestone more efficiently.

5 From the teachings of the aforementioned U.S. patents, it is thus apparent that the utilization of spent ash from a circulating fluidized bed system can be enhanced by hydration or even simple size reduction followed by the reinjection of the spent ash into the combustor of the circulating fluidized bed system in order to thereby achieve additional  
10 sulfation of the reinjected spent ash. Moreover, it is apparent from the teachings of the foregoing U.S. patents that it is possible to realize even additional sulfation through the proper selection of the location whereat the spent ash is reinjected into the circulating fluidized bed system. In addition to those which form the subject matter of the aforementioned U.S.  
15 patents, there are also known to exist in the prior art other ash activation/injection processes. Considered collectively, all of these ash activation/injection processes, for ease of reference, may be categorized as follows: direct spent ash reinjection with no treatment of the spent ash; mechanical grinding of the spent ash in order to expose unreacted CaO  
20 prior to the spent ash being reinjected; humidification of the flue gases without any spent ash recycle; injection of the sorbent into flue gases without any spent ash recycle; reinjection in dry form of hydrated spent ash; reinjection in moist form of hydrated spent ash; and reinjection in slurry form of hydrated spent ash.

25 Although generally speaking these ash activation/injection processes have been demonstrated to be operative for their intended purpose, there has nevertheless been evidenced in the prior art a need for such ash activation/injection processes to be further improved. Namely, there has been evidenced in the prior art a need for a new and improved  
30 method for enhancing the capture of the SO<sub>2</sub> that is released during the combustion of fossil fuel within a fossil fuel-fired combustor, and, in

- 6. -

particular, a new and improved method for reactivating for purposes of the reuse thereof the sorbent, which is injected into the combustor of a circulating fluidized bed system in order to effectuate the capture therewith of the  $\text{SO}_2$  that is released during the combustion of fossil fuel within the combustor of the circulating fluidized bed system.

To this end, there has been evidenced in the prior art a need for such a new and improved method for reactivating sorbent for purposes of the reuse thereof that is characterized in a number of respects. One such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would enable a substantial reduction to be realized in the amount of limestone that would otherwise be required to be utilized to achieve the same amount of  $\text{SO}_2$  capture, i.e., enables a lower Ca/S ratio to be utilized than that which has heretofore been required to achieve the same amount of  $\text{SO}_2$  capture.

Another such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would enable a substantial reduction to be realized in the amount of spent ash that otherwise would be required to be disposed of. A third such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would enable a substantial reduction to be realized in the amount of Ca present in the spent ash that eventually must be disposed of thereby enabling the spent ash to be more readily disposed of. A fourth such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would be capable of implementation without requiring any process modifications to be made in the combustion process by which fossil fuel is burned in fossil fuel-fired combustors and from whence is released the  $\text{SO}_2$ , the capture of which is effected with sorbent. A fifth such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would be capable of implementation without requiring any significant equipment modifications to be made in the fossil fuel-fired



- 7 -

combustors in which the fossil fuel is burned and from whence is released the  $\text{SO}_2$ , the capture of which is effected with sorbent. A sixth such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would be capable of utilization  
5 with virtually any form of fossil fuel-fired combustor in which fossil fuel is burned and from whence is released the  $\text{SO}_2$ , the capture of which is effected with sorbent. A seventh such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would be suitable for application in new fossil fuel-fired  
10 combustors. An eighth such characteristic is that such a new and improved method for reactivating sorbent for purposes of the reuse thereof would be suitable to be retrofitted for application in existing fossil fuel-fired combustors.

It is, therefore, an object of the present invention to provide a  
15 new and improved method for reactivating for purposes of the reuse thereof the sorbent containing unreacted  $\text{CaO}$ , which is injected into a fossil fuel-fired combustor in order to effectuate the capture therewith of the  $\text{SO}_2$  that is released during the combustion of the fossil fuel within the fossil fuel-fired combustor.

20 It is another object of the present invention to provide a new and improved method that is particularly suited to being utilized for reactivating for purposes of the reuse thereof the sorbent containing unreacted  $\text{CaO}$ , which is injected into the combustor of a circulating fluidized bed system in order to effectuate the capture therewith of the  
25  $\text{SO}_2$  that is released during the combustion of fossil fuel within the combustor of the circulating fluidized bed system.

It is still another object of the present invention to provide a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted  $\text{CaO}$ , which is characterized in that  
30 through the use thereof a substantial reduction is enabled to be realized in

- 8 -

the amount of sorbent that would otherwise be required to be utilized to achieve the same amount of SO<sub>2</sub> capture.

Another object of the present invention is to provide such a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized in that  
5 through the use thereof a substantial reduction is enabled to be realized in the amount of spent ash that otherwise would be required to be disposed of.

A still another object of the present invention is to provide  
10 such a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized in that through the use thereof a substantial reduction is enabled to be realized in the amount of Ca present in the spent ash that eventually must be disposed of thereby enabling the spent ash to be more readily  
15 disposed of.

A further object of the present invention is to provide such a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized in that the implementation thereof does not require any process modifications to  
20 be made in the combustion process by which fossil fuel is burned in fossil fuel-fired combustors and from whence is released the SO<sub>2</sub>, the capture of which is effected with sorbent.

A still further object of the present invention is to provide such a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized in  
25 that the implementation thereof does not require any significant equipment modifications to be made in the fossil fuel-fired combustor in which the fossil fuel is burned and from whence is released the SO<sub>2</sub>, the capture of which is effected with sorbent.

Yet an object of the present invention is to provide such a  
30 new and improved method for reactivating for purposes of the reuse

thereof sorbent containing unreacted CaO, which is characterized in that the utilization thereof may be with virtually any form of fossil fuel-fired combustor in which fossil fuel is burned and from whence is released the SO<sub>2</sub>, the capture of which is effected with sorbent.

5 Yet a further object of the present invention is to provide such a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized by its suitability for application in new fossil fuel-fired combustors.

10 Yet another object of the present invention is to provide such a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized by its suitability to be retrofitted for application in existing fossil fuel-fired combustors.

#### 15 SUMMARY OF THE PRESENT INVENTION

In accordance with the present invention there is provided a method for reactivating for purposes of the reuse thereof the sorbent containing unreacted CaO, which is injected into a fossil fuel-fired combustor in order to effectuate the capture therewith of the SO<sub>2</sub> that is released during the combustion of the fossil fuel within the fossil fuel-fired combustor. More specifically, in accord with the subject method of the present invention for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, such reactivation of the sorbent containing unreacted CaO is effected through steam reactivation. To this end, spent ash, which is derived from the combustion of fossil fuel in a fossil fuel-fired combustor and which has present therein particles of sorbent containing unreacted CaO, is subjected to steam, which is at a predetermined temperature and a predetermined partial pressure. As a consequence of this subjection of the spent ash to steam, the unreacted CaO contained in the sorbent particles present in the spent ash is converted to Ca(OH)<sub>2</sub> by virtue of the reaction of the CaO contained in the sorbent particles with the

- 10 -

steam. Moreover, because the volume of  $\text{Ca(OH)}_2$  is greater than the volume of  $\text{CaO}$ , this increase in volume results in a fracturing of the sorbent particles, which had previously contained unreacted  $\text{CaO}$  but which now contain  $\text{Ca(OH)}_2$ , such that by virtue of the fracturing of the sorbent particles the  $\text{Ca(OH)}_2$  thereof becomes exposed. After having  
5 been so exposed to steam, in accord with the subject method of the instant invention the spent ash now having present therein sorbent particles containing  $\text{Ca(OH)}_2$  rather than unreacted  $\text{CaO}$  is then reinjected into the fossil fuel-fired combustor whence the spent ash was derived. To  
10 this end, the spent ash now having present therein sorbent particles containing  $\text{Ca(OH)}_2$  is reinjected into the fossil fuel-fired combustor at a location thereof whereat the temperature is sufficiently high, i.e., in excess of 580 degrees C., so as to cause the  $\text{Ca(OH)}_2$  contained in the sorbent particles present in the reinjected spent ash to covert once again to  $\text{CaO}$   
15 such that by virtue of this reactivation thereof the sorbent present in the reinjected spent ash is rendered once again operative to effectuate the capture therewith of  $\text{SO}_2$  that is released during the combustion of fossil fuel within the fossil fuel-fired combustor.

## 20 BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a side elevational view of one form of fossil fuel-fired combustor, i.e., a circulating fluidized bed system, with which the method of the present invention may be employed;

Figure 2 is a graphical depiction of the disassociation  
25 pressure of  $\text{Ca(OH)}_2$  as a function of temperature based on thermodynamic considerations; and

Figure 3 is a graphical depiction of the conversion of hydrated fly ash with  $\text{SO}_2$ .

## DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawing, and more particularly to Figure 1 thereof, there is depicted therein a form of fossil fuel-fired system generator with which the method of the present invention is capable of being utilized. More specifically, in accord with the best mode embodiment of the invention the fossil fuel-fired combustor illustrated in Figure 1 of the drawing comprises a circulating fluidized bed system, generally denoted in Figure 1 by the reference numeral 10. Fossil fuel, which is most frequently in the form of coal, along with sorbent, which is most frequently in the form of limestone, are fed, as indicated by the arrow denoted by the reference numeral 12 in Figure 1, to the combustor, denoted generally in Figure 1 by the reference numeral 14, of the circulating fluidized bed system 10. As indicated by the arrow denoted by the reference numeral 16 in Figure 1, primary fluidizing air, which has been preheated, is fed in known fashion to the air plenum chamber, denoted in Figure 1 by the reference numeral 18, which is located in the bottom of the combustor 14 such as to be positioned below the air distribution plate, denoted in Figure 1 by the reference numeral 20.

Continuing with the description of the circulating fluidized bed system 10 depicted in Figure 1 of the drawing, combustion supporting air, as indicated by the arrow denoted by the reference numerals 22 and 24, is fed into the combustor 14. Ash, which is generated as a consequence of the combustion in the combustor 14 of the fossil fuel introduced at 16 thereinto is removed from the combustor 14 through the pipe, denoted in Figure 1 by the reference numeral 26, and through the ash cooler, denoted in Figure 1 by the reference numeral 28.

The bottom portion, which comprises the primary combustion zone, of the combustor 14 in accordance with conventional practice is normally refractory lined in order to thereby eliminate therefrom high heat losses. On the other hand, in accordance with conventional practice the

- 12 -

upper portion of the combustor 14 normally contains evaporative waterwall tubes in which steam is generated.

The flue gas generated as a consequence of the combustion within the combustor 14 of the fossil fuel introduced at 16 thereinto along with any solids, which may be entrained in the flue gas, are made to flow from the combustor 14 through the duct, denoted in Figure 1 by the reference numeral 30, to the cyclone separator, denoted in Figure 1 by the reference numeral 32. In the cyclone separator 32, the entrained solids are separated from the flue gas. After being separated in the cyclone separator 32 from the flue gas, the solids drop to the bottom of the cyclone separator 32 whereas the flue gas now minus the previously entrained solids flows out of the top, the latter being denoted in Figure 1 of the drawing by the reference numeral 34, of the cyclone separator 32. From the top 34 of the cyclone separator 32, the flue gas now minus the previously entrained solids then flows through the tangential duct, denoted in Figure 1 by the reference numeral 36, to the convective pass, denoted in Figure 1 by the reference numeral 38, of the circulating fluidized bed system 10, wherein in accordance with conventional practice heat exchange surfaces are typically to be found.

Referring again to Figure 1 of the drawing, the circulating fluidized bed system 10 as illustrated therein is further provided on the bottom of the cyclone separator 32 with a J-leg or seal pot, denoted generally by the reference numeral 40 in Figure 1. The function of the J-leg or seal pot 40 is to effect the recirculation of the solids, which are collected in the cyclone separator 32 after the separation thereof from the flue gas, back to the combustor 14 against the pressure present in the combustor 14. Namely, these solids flow down on the inlet side, i.e., on the side, denoted in Figure 1 by the reference numeral 40a, of the J-leg or seal pot 40, up the outlet side, i.e., the side, denoted in Figure 1 by the reference numeral 40b, of the J-leg or seal pot 40, and then back to the combustor 14 through the duct, denoted in Figure 1 by the reference

- 13 -

numeral 42. In accordance with conventional practice, the bottom portion, denoted in Figure 1 by the reference numeral 40c, of the J-leg or seal pot 40 is normally fluidized, by virtue of the injection therein of air, to permit the solids in the J-leg or seal pot 40 to flow therethrough. As is known to those skilled in this art, the difference in solids level between the inlet side 40a thereof and the outlet side 40b thereof corresponds to the pressure differential across the J-leg or seal pot 40. To this end, solids entering the inlet side 40a of the J-leg or seal pot 40 displace the solids flowing into the duct 42 out of the outlet side 40b of the J-leg or seal pot 40.

Continuing, the circulating fluidized bed system 10, in accordance with the illustration thereof in Figure 1 of the drawing, further embodies a solids withdrawal pipe, denoted in Figure 1 by the reference numeral 44, and a solids flow control valve, represented by the arrow identified in Figure 1 by the reference numeral 46. As seen with reference to Figure 1 of the drawing, the solids withdrawal pipe 44 and the solids flow control valve 46 are suitably supported in the lower portion 40c of the J-leg or seal pot 40. The function of the solids withdrawal pipe 44 is to feed the desired portion, as established through operation of the solids flow control valve 46, of the hot recirculating solids from the J-leg or seal pot 40 to the external fluidized bed heat exchanger, denoted in Figure 1 by the reference numeral 48. In known fashion, the external fluidized bed heat exchanger 48 typically consists of one or more compartments, schematically depicted at 48a in Figure 1, with most compartments 48a containing immersed tube bundles (not shown in the interest of maintaining clarity of illustration in the drawing), which are designed to be operative as evaporative and/or reheat and/or superheat and/or economized heat transfer surface. However, some of the compartments 48a may not be provided with immersed tube bundles. The solids, which enter the external fluidized bed heat exchanger 48, are fluidized for purposes of effecting the flow thereof therethrough. During the course of their passage through the external fluidized bed heat exchanger 48 the

solids, as they gradually pass from one to another of the compartments 48a, transfer heat to the heat transfer surfaces housed therewithin. Thereafter, the solids flow out of the external fluidized bed heat exchanger 48 through the outlet pipe, denoted in Figure 1 by the reference numeral 50, and back to the combustor 14.

The solids, which are circulating around the circulating fluidized bed system 10, i.e., through the combustor 14, the cyclone separator 32 and the external fluidized bed heat exchanger 48, consist of a mixture of unreactive fossil fuel ash and particles of sorbent, which are only partially reacted. To this end, the core of these particles of sorbent comprises unreacted  $\text{CaO}$ , whereas the shell or outer layer of these particles of sorbent consist of  $\text{CaSO}_4$ .

A discussion will next be had herein of  $\text{SO}_2$  capture by sorbent in the combustor 14 of the circulating fluidized bed system 10. In this regard, overall  $\text{SO}_2$  capture by sorbent consisting of limestone, which is added to a circulating fluidized bed system, such as the circulating fluidized bed system 10 illustrated in Figure 1 of the drawing, is traditionally described by two consecutive reactions; namely, those of endothermic calcination and exothermic sulfation. Exothermic sulfation is a net reaction and is not to be interpreted as describing reaction mechanisms on a molecular level. The calcination reaction, which is significant above 700 degrees C., creates very porous  $\text{CaO}$  particles. As the sulfation reaction proceeds, the pore structure of  $\text{CaO}$  particles changes, since the molar volume of  $\text{CaSO}_4$  is larger than that of  $\text{CaO}$  and this tends to block the pores near the outer surface of the particle, preventing further diffusion of  $\text{SO}_2$  into the interior of the sorbent particles. Although there are cases of quite uniform sulfation across the particles found in small particles of fly ash from circulating fluidized bed systems, most of this type of heterogeneous reaction is commonly modeled with an unreacted-core model, which makes allowance for the following: diffusion of gaseous  $\text{SO}_2$  to the surface of the solid particle, penetration and



diffusion of  $\text{SO}_2$  through the  $\text{CaSO}_4$  layer to the surface of the unreacted core, and reaction of  $\text{SO}_2$  with sorbent within the core.

Low calcium utilization, typically only 25 to 45%, leads to a relatively large quantity of waste products for disposal. Thus, if the overall utilization of fresh sorbent can be increased, a significant improvement of the desulfurization process, in terms of both economics and pollution control, could be accomplished. As noted herein previously, among the methods that have been found to have the potential to increase the utilization of sorbent significantly is hydration of spent sorbent/ash by steam reactivation at low temperature combined with recirculation of the reactivated sorbent/ash back to the combustor. Enhanced utilization of sorbent by such hydration is attributable to the difference in molar volume of  $\text{CaO}$  and  $\text{Ca(OH)}_2$ . To this end, when spent sorbent/ash is exposed to steam, the strong affinity between water and unreacted  $\text{CaO}$  leads to absorption of water in the pores of the particles so that  $\text{CaO}$  is converted to  $\text{Ca(OH)}_2$ .

In Figure 2 of the drawing the partial pressure of water in equilibrium with a mixture of  $\text{CaO}$  and  $\text{Ca(OH)}_2$  is depicted by means of the curve denoted therein by the reference numeral 52. Thus, the curve 52 effectively represents the minimum partial pressure of water vapor in an environment to effect rehydration of  $\text{CaO}$  as a function of temperature. The curve 52 was computed using free energies of formation and heat capacities of the pure solids and gases. From a reference to Figure 2 of the drawing, it can be seen that hydration is possible at high temperatures, i.e., at temperatures within the range of 250 degrees C. to 700 degrees C. and high  $\text{H}_2\text{O}$  partial pressures up to 1.0 and beyond. Moreover, it can be seen from a reference to Figure 2 of the drawing that  $\text{Ca(OH)}_2$  is stable below 450 degrees C. with a volume percent moisture of 60%. As such, given the smaller size of water vapor molecules compared with  $\text{SO}_2$ , penetration of  $\text{H}_2\text{O}$  to previously unutilized  $\text{CaO}$  sites is therefore feasible. Furthermore, under appropriate conditions in-situ rehydration of  $\text{CaO}$  to

$\text{Ca(OH)}_2$  can be had with a corresponding volume change and concomitantly exposure of unreacted  $\text{CaO}$  surface area, which would then allow further  $\text{SO}_2$  capture when the sorbent particles that have been subjected to such in-situ rehydration of  $\text{CaO}$  are reinjected into a circulating fluidized bed system, e.g., into the combustor 14 of the circulating fluidized bed system 10 illustrated in Figure 1 of the drawing.

Heretofore, the effect of temperature on hydration of partially sulfated limestone has been the subject of several studies. Such studies have found that the conversion of  $\text{CaO}$  to  $\text{Ca(OH)}_2$  decreased when the temperature was increased from 100 degrees C. to 300 degrees C. at a constant moisture content. Further, it was observed in such studies that the rate of hydration increased as the temperature was decreased. Moreover, it was suggested that this was due to the mechanism by which steam reaches active  $\text{CaO}$  sites and proposed that the diffusional resistance toward steam is partially caused by the increase in molar volume resulting from the formation of  $\text{Ca(OH)}_2$ . To this end, it could be that the decrease in both reaction rate and ultimate conversion is caused by pore plugging, similar to that occurring during sulfation, with an increasing temperature causing the pores of the sorbent particles to plug faster.

With further reference to the aforementioned studies, it has been found therefrom that the rate of hydration is much slower with steam than with water. Such studies assumed that this was caused by the transport mechanism of water through the sorbent particles rather than because of pore plugging. To this end, it was suggested in such studies that water molecules are quickly absorbed because of the surface tension of water, which draws water into the pores of the sorbent particles, where the water reacts with the  $\text{CaO}$ .

All the work done in the course of such studies has been carried out at temperatures below 300 degrees C. In these studies, there does not appear to have been any systematic consideration given to

reactivation at temperatures above 300 degrees C., perhaps partially because decomposition of  $\text{Ca(OH)}_2$  becomes significant at 300 degrees C., and thermodynamic as well as kinetic factors become important. In particular, a minimum partial pressure of steam, above the decomposition  
5 pressure of  $\text{Ca(OH)}_2$ , is needed to effect reactivation.

Reference will next be had herein to Figure 3 of the drawing wherein a series of curves, denoted therein by the reference numerals 54, 56 and 58, respectively, are depicted. The trends, which are shown by the curves 54, 56 and 58, can be explained by a combination of  
10 thermodynamic and kinetic factors. Thermodynamic factors enter into this discussion in two ways. First, there is the determination of whether at a given steam partial pressure reactivation can occur at a specified temperature in accord with curve 52 of Figure 2 of the drawing. Secondly, thermodynamic factors have an influence on the reaction rate.

15 It appears that the effect of temperature and steam partial pressure as shown by the curves 54, 56 and 58 in Figure 3 of the drawing is explainable where the rate of reactivation is limited by diffusion of steam through pores in a surface layer of spent ash. To this end, the rate of diffusion is proportional to two temperature dependent factors, i.e., the  
20 diffusion coefficient divided by the temperature, and the driving force. Furthermore, the driving force is equal to the difference in steam partial pressure in the bulk gas and in the center of the sorbent particle (the decomposition pressure). As regards the diffusion coefficient, the diffusion coefficient increases with temperature to a power varying  
25 between approximately 1.5 and 0.5 depending upon whether the diffusion is bulk diffusion or Knudsen diffusion. However, for a given partial pressure of steam, the driving force for diffusion decreases with temperature because of the increase in the steam partial pressure in the center of the sorbent particle. The result of these two counteracting trends  
30 is a maximum in the reactivation rate, provided that the diffusion coefficient varies with temperature to a power greater than unity. The

overall trend, as illustrated by the curves 54, 56 and 58 in Figure 3 of the drawing, shows that the reaction rate increases with temperature to a maximum, because the diffusion coefficient increases. Moreover, at a temperature higher than this maximum point the reaction rate falls off as the driving force falls, reaching zero when the bulk diffusion is equal to the decomposition pressure.

The spent ash, which is to be subjected to steam reactivation in accordance with the method of the present invention may be obtained from several locations in the circulating fluidized bed system 10. Namely, the spent ash, which is to be subjected to steam reactivation in accordance with the present invention may be obtained from the ash cooler 28, or from the J-leg or seal pot 40, or from the external fluidized bed heat exchanger 48. In addition, it is also contemplated in accordance with the method of the present invention that steam reactivation of the spent ash may take place in-situ. That is, steam may be employed to perform a dual function, i.e., to effect the fluidization of the solids being recirculated from the cyclone separator 32 to the combustor 14 while at the same time this same steam is operative to effect the steam reactivation in-situ of the recirculated solids. To this end, as depicted by the arrows denoted by the reference numeral 60 in Figure 1 of the drawing, the steam employed for this purpose may be introduced into the outlet pipe 50 of the circulating fluidized bed system 10. Other than when the steam reactivation of the spent ash takes place in-situ, the spent ash after being subjected to steam reactivation in accordance with the present invention preferably is reintroduced into the combustor 14 at 12 along with the fossil fuel that is to be burned therewithin.

Thus, in accordance with the present invention there has been provided a new and improved method for reactivating for purposes of the reuse thereof the sorbent containing unreacted  $\text{CaO}$ , which is injected into a fossil fuel-fired combustor in order to effectuate the capture therewith of the  $\text{SO}_2$  that is released during the combustion of the fossil

fuel within the fossil fuel-fired combustor. Besides, there has been provided in accord with the present invention a new and improved that is particularly suited to being utilized for reactivating for purposes of the reuse thereof the sorbent containing unreacted  $\text{CaO}$ , which is injected into

5 the combustor of a circulating fluidized bed system in order to effectuate the capture therewith of the  $\text{SO}_2$  that is released during the combustion of fossil fuel within the combustor of the circulating fluidized bed system. As well, in accordance with the present invention there has been provided a new and improved method for reactivating for purposes of the reuse

10 thereof sorbent containing unreacted  $\text{CaO}$ , which is characterized in that through the use thereof a substantial reduction is enabled to be realized in the amount of sorbent that would otherwise be required to be utilized to achieve the same amount of  $\text{SO}_2$  capture. Moreover, there has been provided in accord with the present invention a new and improved method

15 for reactivating for purposes of the reuse thereof sorbent containing unreacted  $\text{CaO}$ , which is characterized in that through the use thereof a substantial reduction is enabled to be realized in the amount of spent ash that otherwise would be required to be disposed of. Also, in accordance with the present invention there has been provided a new and improved

20 method for reactivating for purposes of the reuse thereof sorbent containing unreacted  $\text{CaO}$ , which is characterized in that through the use thereof a substantial reduction is enabled to be realized in the amount of Ca present in the spent ash that eventually must be disposed of thereby enabling the spent ash to be more readily disposed of. Further, there has

25 been provided in accord with the present invention a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted  $\text{CaO}$ , which is characterized in that the implementation thereof does not require any process modifications to be made in the combustion process by which fossil fuel is burned in fossil

30 fuel-fired combustors and from whence is released the  $\text{SO}_2$ , the capture of which is effected with sorbent. In addition, in accordance with the present

invention there has been provided a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized in that the implementation thereof does not require any significant equipment modifications to be made in the fossil fuel-fired combustor in which the fossil fuel is burned and from whence is released the SO<sub>2</sub>, the capture of which is effected with sorbent. Furthermore, there has been provided in accord with the present invention a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized in that the utilization thereof may be with virtually any form of fossil fuel-fired combustor in which fossil fuel is burned and from whence is released the SO<sub>2</sub>, the capture of which is effected with sorbent. Penultimately, in accordance with the present invention there has been provided a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized by its suitability for application in new fossil fuel-fired combustors. Finally, there has been provided in accord with the present invention a new and improved method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO, which is characterized by its suitability to be retrofitted for application in existing fossil fuel-fired combustors.

What is claimed is:

1. In a fossil fuel-fired combustor wherein sorbent containing Ca is injected for purposes of effecting the capture therewith of SO<sub>2</sub> released during the combustion of fossil fuel in the fossil fuel-fired combustor, the improvement of a method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO comprising the steps of:
  - a. providing a supply of spent ash embodying sorbent containing unreacted CaO, the spent ash having been generated as a consequence of the combustion in the fossil fuel-fired combustor of the fossil fuel in the presence of the sorbent containing Ca;
  - b. subjecting the supply of spent ash embodying sorbent containing unreacted CaO to steam having a predetermined temperature and a predetermined partial pressure operative to effect the conversion to Ca(OH)<sub>2</sub> of the unreacted CaO contained in the sorbent embodied in the spent ash such that as a consequence of Ca(OH)<sub>2</sub> having a greater volume than CaO a fracturing of the sorbent occurs thereby exposing the Ca(OH)<sub>2</sub>;
  - c. reinjecting into the fossil fuel-fired combustor the spent ash embodying the sorbent containing the Ca(OH)<sub>2</sub> at a temperature within the fossil fuel-fired combustor operative to effect the conversion to CaO of the Ca(OH)<sub>2</sub> contained in the sorbent embodied in the reinjected spent ash; and
  - d. effecting with the sorbent containing the reconverted CaO the capture of SO<sub>2</sub> released during the combustion of fossil fuel in the fossil fuel-fired combustor.
2. In a fossil fuel-fired combustor, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 1 wherein the supply of spent ash embodying

- 22 -

sorbent containing unreacted CaO is subjected to steam having a temperature in the range of 250 degrees C. to 700 degrees C.

3. In a fossil fuel-fired combustor, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 2 wherein the supply of spent ash embodying sorbent containing unreacted CaO is subjected to steam having a partial pressure in the range of 0.0 to 1.2.
4. In a fossil fuel-fired combustor, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 1 wherein the spent ash embodying the sorbent containing the  $\text{Ca}(\text{OH})_2$  is reinjected into the fossil fuel-fired combustor at a temperature within the fossil fuel-fired combustor in excess of 580 degrees C.
5. In a fossil fuel-fired combustor, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 1 wherein the supply of spent ash embodying sorbent containing unreacted CaO is subjected to steam externally of the fossil fuel-fired combustor.
6. In a fossil fuel-fired combustor, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 1 wherein the supply of spent ash embodying sorbent containing unreacted CaO is subjected to steam in-situ.
7. In a circulating fluidized bed system including a combustor, a cyclone separator and a heat exchanger wherein sorbent containing Ca is injected into the combustor of the circulating fluidized bed system for purposes of effecting the capture therewith of  $\text{SO}_2$  released during the combustion of fossil fuel in the combustor of the circulating fluidized bed system, the improvement of a method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO comprising the steps of:



- 5 a. providing a supply of spent ash embodying sorbent containing unreacted CaO, the spent ash having been generated as a consequence of the combustion in the combustor of the circulating fluidized bed system of fossil fuel in the presence of sorbent containing Ca;
- 10 b. subjecting the supply of spent ash embodying sorbent containing unreacted CaO to steam having a predetermined temperature and a predetermined partial pressure operative to effect the conversion to  $\text{Ca(OH)}_2$  of the unreacted CaO contained in the sorbent embodied in the spent ash such that as a consequence of  $\text{Ca(OH)}_2$  having a greater volume than CaO a fracturing of the sorbent occurs thereby exposing the  $\text{Ca(OH)}_2$ ;
- 15 c. reinjecting into the combustor of the circulating fluidized bed system the spent ash embodying the sorbent containing the  $\text{Ca(OH)}_2$  at a temperature within the combustor of the circulating fluidized bed system operative to effect the conversion to CaO of the  $\text{Ca(OH)}_2$  contained in the sorbent embodied in the spent ash; and
- 20 d. effecting with the sorbent containing the reconverted CaO the capture of  $\text{SO}_2$  released during the combustion of fossil fuel in the combustor of the circulating fluidized bed system.
- 25 8. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 7 wherein the supply of spent ash embodying sorbent containing unreacted CaO is subjected to steam having a temperature in the range of 250 degrees C. to 700 degrees C.
- 30 9. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 8 wherein the supply of spent ash embodying

sorbent containing unreacted CaO is subjected to steam having a partial pressure in the range of 0.0 to 1.2.

10. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 7 wherein the spent ash embodying the sorbent containing the  $\text{Ca(OH)}_2$  is reinjected into the combustor of the circulating fluidized bed system at a temperature within the combustor of the circulating fluidized bed system in excess of 580 degrees C.
11. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 7 wherein the supply of spent ash embodying sorbent containing unreacted CaO is obtained from the combustor of the circulating fluidized bed system.
12. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 7 wherein the supply of spent ash embodying sorbent containing unreacted CaO is obtained from the cyclone separator of the circulating fluidized bed system.
13. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 7 wherein the supply of spent ash embodying sorbent containing unreacted CaO is obtained from the heat exchanger of the circulating fluidized bed system.
14. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as set forth in Claim 7 wherein the supply of spent ash embodying sorbent containing unreacted CaO is subjected to steam externally of the circulating fluidized bed system.
15. In a circulating fluidized bed system, the method for reactivating for purposes of the reuse thereof sorbent containing unreacted CaO as

set forth in Claim 7 wherein the supply of spent ash embodying sorbent containing unreacted CaO is subjected to steam in-situ.

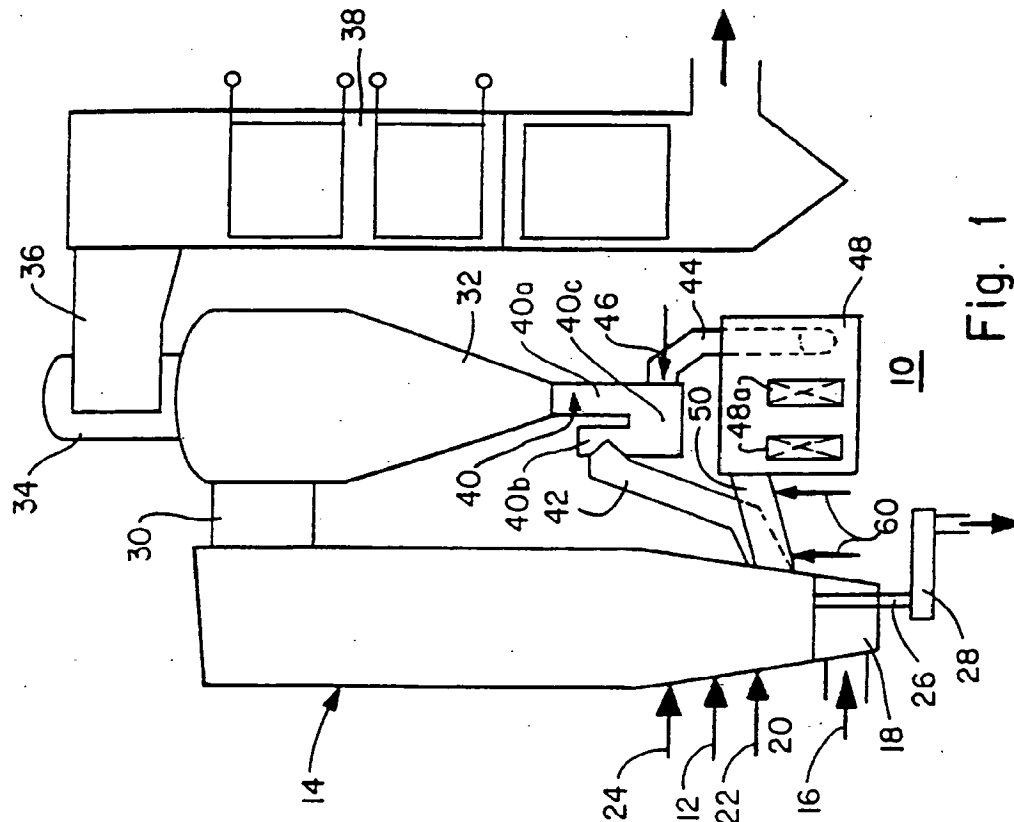


Fig. 1

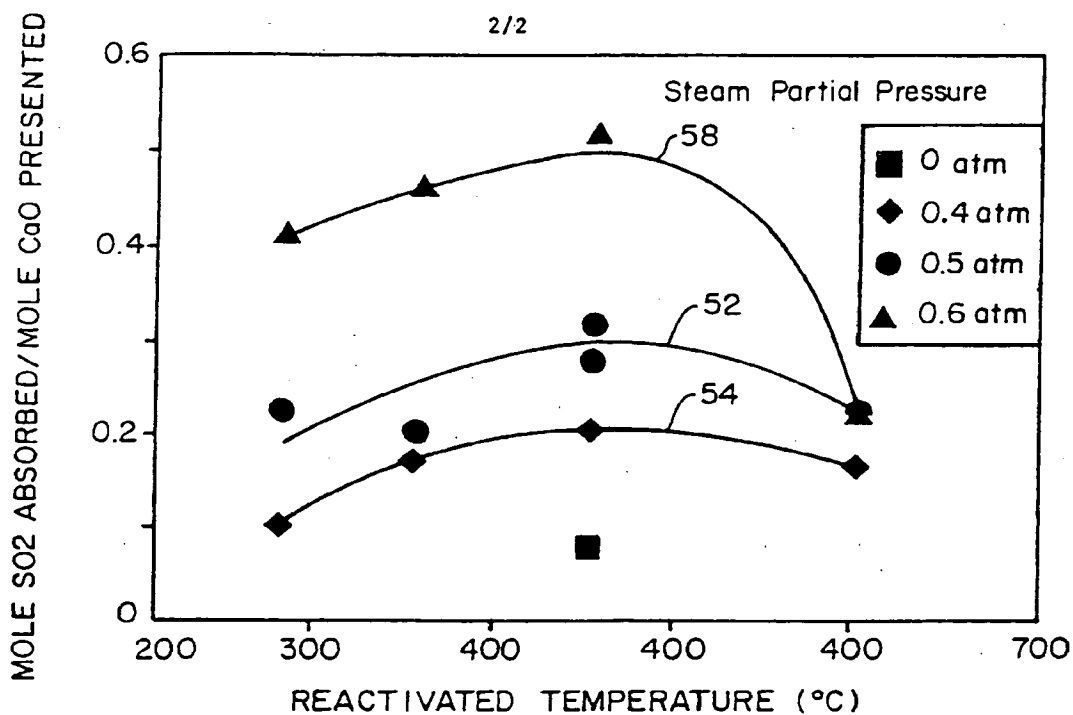


Fig. 3

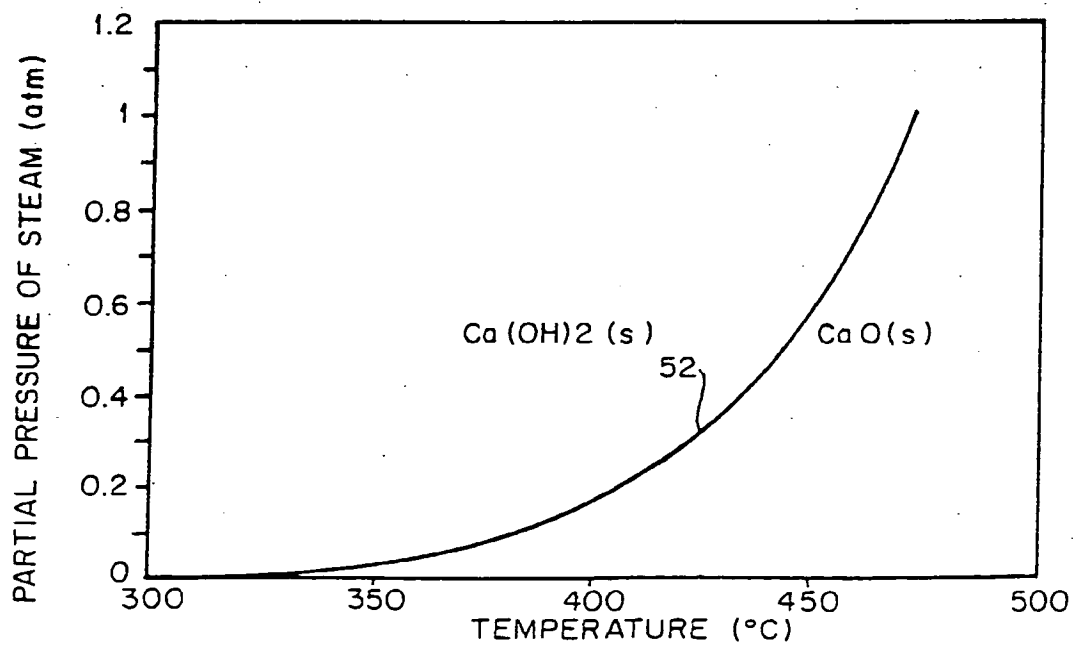


Fig. 2

## INTERNATIONAL SEARCH REPORT

International Application No.

PC 1/1B 96/00930

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J20/34 B01D53/50 F23C11/02 F23L7/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J B01D F23C F23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 312 280 (SHEARER) 26 January 1982 " IN TOTALITY "	1-6
Y	US,A,4 872 423 (PILLAI) 10 October 1989 " IN TOTALITY "	1-15
Y	US,A,5 345 883 (PANOS) 13 September 1994 cited in the application " IN TOTALITY "	1-15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*A\* document member of the same patent family

Date of the actual completion of the international search

6 December 1996

Date of mailing of the international search report

20.12.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Wendling, J-P

Form PCT/ISA/210 (second sheet) (July 1992)

BEST AVAILABLE COPY

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/IB 96/00930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4312280	26-01-82	NONE	
US-A-4872423	10-10-89	SE-B- 457014	21-11-88
		DE-A- 3880878	17-06-93
		DE-T- 3880878	11-11-93
		EP-A- 0287815	26-10-88
		JP-A- 63254305	21-10-88
		SE-A- 8701229	26-09-88
US-A-5345883	13-09-94	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)

BEST AVAILABLE COPY